

# TIME RESOLVED MICROWAVE REFLECTIVITY STUDIES ON THE PHOTODISSOLUTION OF n-Si IN FLUORIDE SOLUTIONS

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Interfacial electron transfer processes at electrodes are normally characterized by electrical measurements. In the case of semiconductor electrodes under illumination, the net rate of electron transfer is evident from the measured photocurrent. The problem is that the photocurrent gives no information about the rate *constant* for electron transfer because the concentration of electrons or holes at the interface is not known a priori. In the simplest case, the photocurrent is just determined by the absorbed photon flux. Photogenerated carriers may react quickly, so that their concentration remains small. On the other hand they may react more slowly so that a larger concentration builds up. In effect, carriers can ‘queue’ at the interface. These carriers can be detected using microwave reflectivity method pioneered by Tributsch and coworkers<sup>1</sup>. The technique involves detecting the small changes in conductivity associated with the build up of carriers at the interface. We have developed and extended this technique to follow photoelectrochemical processes in the time and frequency domain, and work is in progress on detailed theoretical modeling of the microwave response. The microwave response is related to the photocurrent response, which is measured simultaneously (Fig 1).

In this contribution we present recent results obtained for n-type silicon. The photoelectrochemical dissolution of n-Si in fluoride solutions is complex, involving electron injection steps in addition to hole capture<sup>2</sup>. The microwave techniques are providing new insights into the kinetics and mechanisms of these processes.

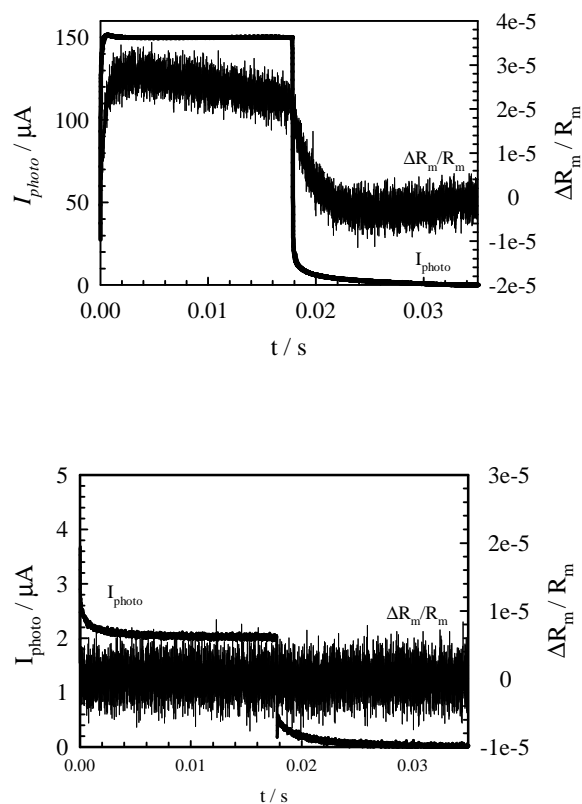
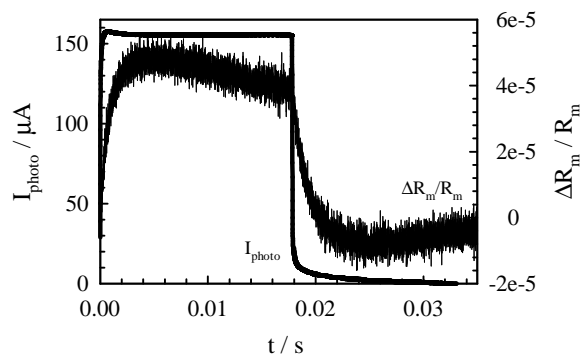


Figure 1: Time resolved microwave reflectivity and photocurrent measurements on n-Si(111) in a 1M fluoride solution adjusted to pH 3. Illuminated using a chopped (frequency of 57Hz) green He-Ne laser (543nm) under depletion conditions (a, b) and near the flat band potential (c).

1. G.Schlichthörl and H. Tributsch. *Electrochim. Acta* **37**, 919 (1992). H. Tributsch, G. Schlichthörl and L. Elstner, *Electrochim. Acta* **38**, 141 (1993).
2. L.M. Peter, *Chem. Rev.* **90**, 753 (1992).